

Chromophoric Dissolved Organic Matter In Coastal Waters

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LONG-TERM GOAL

It is the goal of this proposal to evaluate our understanding of CDOM sources and distributions in coastal waters by comparing high-resolution observations with four-dimensional, physical, chemical and biological models of the CDOM fields.

OBJECTIVES

- 1.) Study the freshwater CDOM endmember variability due to watershed and rainfall properties by monitoring Hudson River, Mississippi River, Neponset River, and Parker River endmembers.
- 2.) Determine the seasonal influence of salt marshes on estuarine CDOM fluxes.
- 3.) Determine high-resolution spatial and temporal variability of CDOM and other relevant parameters in the Hudson River Mouth/New Jersey Shelf region.
- 4.) Adapt Paul Bissett's (Florida Environmental Research Institute) Ecological Simulation model to the Hudson River Mouth/New Jersey shelf region by hindcasting ECOShuttle CDOM measurements.
- 5.) Study the processes driving the sources and distribution of CDOM by comparing model predictions with observations.
- 6.) Study the effects of photodegradation and biodegradation on CDOM using stable and radiocarbon isotopes, incubations, and models.

APPROACH

Freshwater CDOM source variability will be carried out by deploying SeaPoint CDOM fluorometers at several freshwater locations: the Mississippi, Atchafalaya, Hudson, Neponset, and Parker Rivers.

A major CDOM source appears to be natural wetlands/salt marshes where estuarine water exchanges with porewater in the tidal salt marsh yielding a mid-estuary CDOM source. Intense tidal mixing and multiple salt marsh inputs (groundwater, overland flow, porewater exchange) make quantification of the salt marsh fluxes difficult, but with continued high-resolution Mini-Shuttle observations in the

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Neponset and Plum Island estuaries, isotopic measurements (DO^{13}C), and the well systems established at the Plum Island Ecosystems LTER, we will further refine these sources. Current estimates suggest that 50-90% of the CDOM exported from the Parker River are derived from the marsh.

We proposed a single 5-day cruise in the summer of 2003 and two 5-day cruises in the summer of 2004 with the Integrated Coastal Observation System (ICOS). This uses the ECOShuttle, the winch and the attached 20' lab van with computers flow-through instruments, data acquisition system, and control hardware and software. We will initially concentrate on crossing the shelf 5 times (100 km across shelf every 50 km for a 100 x 200 km study area) for maximum coverage of the plume to initiate the Ecological Simulation model. Traveling at 8 knots, this 900 km ship track requires about 70 hours. Additionally, for continuous surface coverage the Mini-Shuttle with its reduced instrument suite (CDOM, T, S, DO, Chl) will be deployed over the side of the ship (out of the ship's wake) at 1 meter depth. This will provide high spatial resolution for satellite data. A Teflon sampling tube and Teflon diaphragm pump will allow discrete samples be taken from the Mini-Shuttle as well.

The Ecological Simulator (EcoSim 2.0) model simulates the hyperspectral bio-optical properties of the water column via a size-fractionated phytoplankton community, and includes constituents of labile and refractory CDOM (Bissett et al., 1999; 2001a; b). Year 1 data will be used to hindcast CDOM distributions with observations. We will highlight those areas where uncertainty is high, where certain parameters are highly significant, and where higher temporal or spatial observations are needed.

Our recent radiocarbon and stable carbon isotope measurements on high molecular weight DOM (HMW-DOM) samples isolated from several estuarine and coastal waters indicate that distinct differences in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ exist among the major organic compound classes: amino acids, carbohydrates and lipids in these HMW-DOM samples (Wang, submitted). Carbohydrate and amino acid fractions had much younger ^{14}C ages and heavier $\delta^{13}\text{C}$ signatures than that of lipid fraction. Since these organic compound fractions have different influence to the fluorescence of CDOM, it would be interesting to determine which fraction of CDOM (labile vs. refractory; young vs. old) is degraded photo-chemically and biologically. In this study, we will use both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements to seek answers to this important problem.

WORK COMPLETED

A major effort in Year 1 was to prepare the ICOS van for its maiden voyage. The van was built, instruments were mounted permanently, and a new data acquisition protocol was developed. Currently, all data is passed from individual computers that control individual instruments to a central computer that files the data in ASCII format in a single time-stamped spreadsheet. This acts for automatic backup of all data acquired. The van is wired with Ethernet to allow all computers to have synchronized clocks and communicate freely. A final computer is designed to manipulate, visualize and enter data into a database. This data manipulation is a focus of year 2. Additionally, a flowing seawater system was developed to distribute pumped seawater from the surface (MiniShuttle or ship's pumping system) and depth (ECOShuttle) to all the various onboard instruments including the AC-9, the TOCN analyzer, time-resolved laser-induced fluorescence system, the LISST-100, and the 3-nutrient analyzers. All of these instruments were placed on-line during the maiden voyage. We completed a 5-day research cruise with the ICOS van, ECOShuttle, MiniShuttle, and data system in June (19-23), 2003 on the RV Oceanus. Data from the ECOShuttle, MiniShuttle, and all in-line

instruments has been collected and is currently being analyzed, examples of which are shown in Figures 1 and 2.

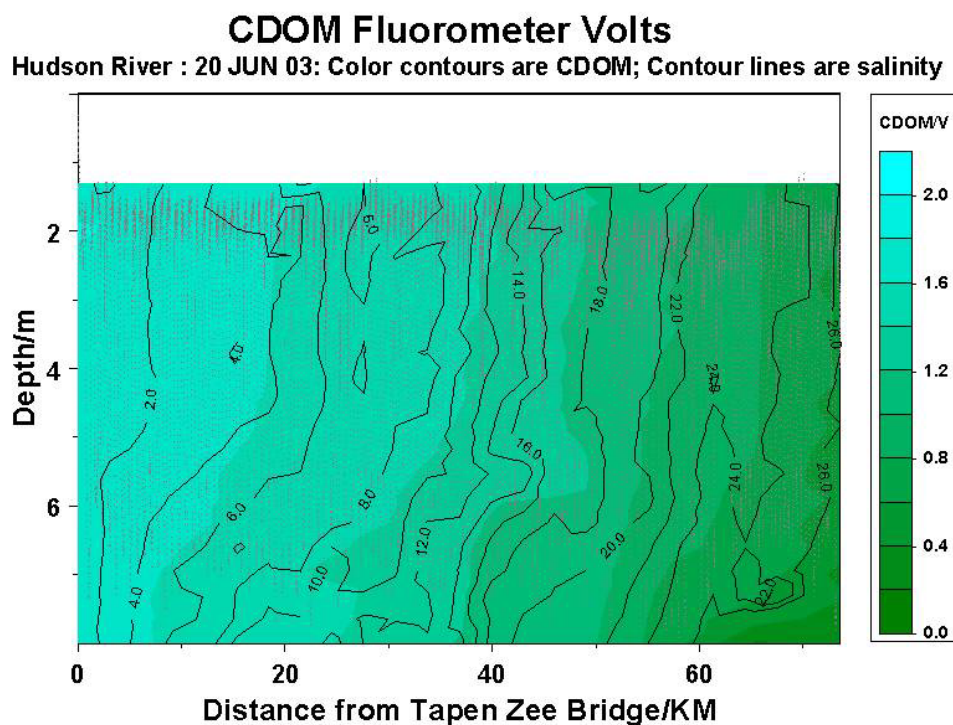


Figure 1: CDOM fluorescence in the Hudson River showing higher fluorescence upstream and lower CDOM, higher salinity water forming a wedge underneath and seaward of the fresher water.

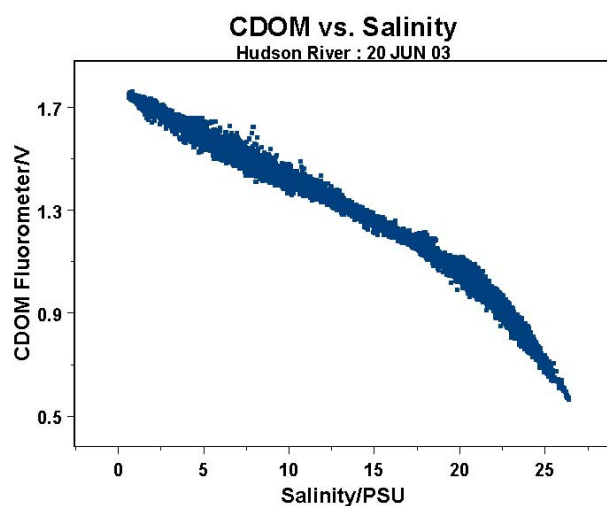


Figure 2: CDOM fluorescence vs. salinity for the Hudson River Transect showing a distinct bend at about 20 ppt where the Hudson River widens into Hudson Bay.

Additionally, we have developed a stand-alone SeaTech CDOM fluorometry system for monitoring freshwater endmember CDOM variations. The prototype instrument is currently deployed in the

Mississippi River. Data and discrete samples have been gathered. A second instrument has been built for the Neponset River, but is awaiting some mechanical parts to against vandalism.

RESULTS

Results so far from our field activities have yielded some important findings:

- 1.) CDOM fluorescence is not simply driven by conservative mixing of a freshwater endmember and seawater. Careful analysis of the Neponset River estuary data has shown localized inputs from salt marshes and complex mixing patterns.
- 2.) The fluorescence-Salinity relationship in the Hudson River estuary suggests a source of CDOM just shoreward of Manhattan in Hudson Bay. There is a major break between apparent freshwater endmembers in the Hudson River and Estuary water and coastal seawater just outside the mouth of the estuary. We propose that the shallow estuary with inputs from the Raritan act as a reactor vessel and add or alter CDOM properties before the Hudson River Plume exits onto the shelf.
- 3.) There is a turbidity front approximately 40 km downstream from the Tappan Zee Bridge where the optical backscatter drops dramatically. A chlorophyll fluorescence maximum is apparent just outside the Hudson estuary on the shelf suggesting a temporal or spatial offset between water clarity (light levels) and phytoplankton growth.
- 4.) Freshwater CDOM endmembers can change significantly (~30%) over the course of weeks in the Mississippi River.

IMPACT/APPLICATIONS

High resolution optical measurements along with auxiliary data allow a much better understanding of complex coastal processes. The ICOS van allows simultaneous collection of the necessary data to initiate existing models for the coastal environment. Our data shows processes in the Hudson and Mississippi similar to the other estuaries that we have studied. Careful interpretation of all these data from several estuaries will better allow a model to be applied to the Hudson and tested.

TRANSITIONS

The initial cruise data will serve to guide 2 cruises in Year 2 as well as 4 cruises in the same area (1 proposed for 2004, 2 proposed for 2005, 1 proposed for 2006) for an NSF sponsored Coastal Ocean Processes project entitled LATTE (Lagrangian Transport and Transformation Experiment).

The results obtained so far have led to discussions with scientists at Rutgers, University of Georgia, the Marine Biological Laboratory in Woods Hole, and numerous others. The comparisons between diverse estuaries should yield far-reaching conclusions that can be used by these and other estuarine researchers. The ECOShuttle and ICOS van have not yet been used for other projects, but will be used for LATTE and proposals to use it to study krill overwintering in a Norwegian Fjord are pending. The Mini-Shuttle has been used to study natural hydrocarbon seeps off Santa Barbara, California, as well as the Apalachicola estuary. Juanita Urban-Rich, Diane McKnight and I organized a Special Session

at the ASLO meeting in Salt Lake City, February of 2003 on Discrete sources of DOM in the aquatic systems.

RELATED PROJECTS

- 1.) Our DURIP project to increase observational capabilities with our Integrated Coastal Observation System (ICOS) has been completed to meet the needs of this proposal.
- 2.) An NSF sponsored Coastal Ocean Processes project entitled LATTE (Lagrangian Transport and Transformation Experiment), Bob Chant, Rutgers, PI, has begun and will use this project's data to drive sampling and observation strategies. Data from both projects will be shared to meet common objectives including high resolution mapping, coastal transport and transformation processes in the Hudson River/New Jersey Shelf region, and application of the ECOSim 2.0 model.
- 3.) Juanita Urban-Rich is studying zooplankton effects on CDOM in coastal waters. We are sharing samples and developing the ICOS van and ECOShuttle capabilities to support a video plankton recorder along with all our integrated data set.
- 4.) Dan Repeta, is studying the production of discrete CDOM components by phytoplankton in culture (ONR funded). Phytoplankton produced DOM is extracted by solid phase extraction (C_{18}) and examined by 1H NMR. Fluorescent EEMs are also measured of the several cultures at various growth phases to examine the production of CDOM components.

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